## The Effect of Nano-Sized Metal Deposits on $TiO_2$ on the Photocatalytic Activity and Mechanism

Wonyong Choi, Eun Young Bae, Jae Sang Lee, and Soonhyun Kim

## School of Environmental Science and Engineering Pohang University of Science and Technology Pohang, 790-784, Korea

 $TiO_2$  photocatalysis has been extensively studied for its environmental applications and demonstrated to be a technically viable clean-up process (1). The main drawbacks of the low quantum yields and the lack of visible-light utilization, however, hinder its widespread acceptance as a practical remediation technology. Various approaches have been attempted to enhance the photocatalytic efficiency of TiO<sub>2</sub>, which include metal-ion doping, metallization, and sensitization.

In this study, we investigated and compared the effects of depositing nano-sized metal particles (M: Pt, Au) on  $TiO_2$  in three different aquatic photocatalytic systems: (1) dye-sensitized M/TiO<sub>2</sub> for the visible light photocatalytic degradation of perchlorinated compounds, (2) M/TiO<sub>2</sub> photocatalyst for ammonia removal, and (3) M/TiO<sub>2</sub> photocatalyst for trichloroacetate (TCA) degradation. The Pt and Au particles were photodeposited on  $TiO_2$  (Degussa P25) with a typical loading of ca. 0.2 wt%. The transmission electron microscopic (TEM) images showed that Pt particles with a size range of 1-2 nm were well dispersed on  $TiO_2$  particles (20-30 nm diameter).

Figure 1 exhibits the dramatic effect of the platinization of the sensitized  $TiO_2$  on the visible light-induced dechlorination of  $CCl_4$ . The dechlorination initiates by the conduction band electron transfer to  $CCl_4$  (2).

 $\text{CCl}_4 + e_{cb}^{-}(\text{Pt}) \rightarrow \text{\bullet}\text{CCl}_3 + \text{Cl}^{-}$ 

The presence of Pt deposits on  $\text{TiO}_2$  in this case reduces the fast back electron transfer to the oxidized dye and enhances the interfacial electron transfer to CCl<sub>4</sub>. The Pt/TiO2 was also very effective in photocatalytic denitrification of ammonia as shown in Figure 2. While the pure TiO<sub>2</sub> almost quantitatively transformed ammonia into nitrite and nitrate (Fig. 2a), Pt/TiO<sub>2</sub> converted NH<sub>3</sub> into N<sub>2</sub> with reducing the total nitrogen concentration in the suspension (Fig. 2b). The evolution of  $N_2$  gas was confirmed by detecting  ${}^{30}N_2$  using GC/MS from  ${}^{15}NH_3$ conversion. Au/TiO2 did not exhibit such denitrification effect. The photocatalytic degradation of TCA on Pt/TiO<sub>2</sub> was significantly different from that on pure TiO<sub>2</sub> with showing different product distribution. In the above three photocatalytic systems, both the photocatalytic activity and mechanism changed when Pt was deposited on TiO<sub>2</sub>. Although the platinization of TiO<sub>2</sub> has been widely studied, its effect on the photocatalytic mechanism is not well understood. The role of metals and their effect on the photocatalytic reaction system will be discussed.

## REFERENCES

1. M. R. Hoffmann, S. T. Martin, W. Choi, D. W. Bahnemann, *Chem. Rev.*, **95**, 69 (1995).

2. Y. Cho, W. Choi, C.-H. Lee, T. Hyeon, H.-I. Lee, *Environ. Sci. Technol.*, **35**, 966 (2001).



**Figure 1.** Chloride production from  $CCl_4$  degradation on  $TiO_2/Ru^{II}L_3$  and  $Pt/TiO_2/Ru^{II}L_3$  under visible light illumination. The experimental conditions were:  $[TiO_2] = 0.5 \text{ g/L}$ ,  $[Ru^{II}L_3]_i = 10 \text{ }\mu\text{M}$ ,  $[CCl_4]_i = 1 \text{ }m\text{M}$ ,  $pH_i = 3$ , and initially N<sub>2</sub>-saturated.



**Figure 2**. Photocatalytic degradation of  $NH_3$  on (a) pure  $TiO_2$  and (b)  $Pt/TiO_2$  under UV irradiation. The experimental conditions were  $[NH_3]_0 = 100 \ \mu M$ ,  $[TiO_2] = 0.5 \ g/L$ , pH = 10, and air-equilibrated.